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(54) Title: METHOD OF GENERATING A REACTIVE SPECIES AND APPLICATIONS THEREFOR (57) Abstract A method of generating reactive species which includes exposing a polymolecular photoreactor to radiation, in which the polymolecular photoreactor comprises a wavelength-specific sensitizer associated with a reactive species generating photoinitiator. The sensitizer absorbs energy and transfers the absorbed energy to the photoinitiator which, in turn, generates reactive species. The wavelength-specific sensitizer is adapted to have an absorption wavelength band generally corresponding to an emission peak of the radiation. The radiation to which the polymolecular photoreactor is exposed generally will have a wavelength of from about 4 to about 1,000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation; visible radiation; and near infrared radiation. Desirably, the radiation will have a wavelength of from about 100 to about 900 nanometers. More desirably, in one embodiment, the radiation will have a wavelength of from about 100 to about 375 nanometers, in which case the radiation desirably is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp. Also described are methods of polymerizing unsaturated monomers and curing an unsaturated oligomer/monomer mixture.		

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METHOD OF GENERATING A REACTIVE SPECIES AND APPLICATIONS THEREFOR

Cross-Reference to Related Application

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This application is a continuation-in-part application of U.S. Serial No. 08/268,685, filed on June 30, 1994.

Background of the Invention

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The present invention relates to a method of generating a reactive species. The present invention also relates to radiation-initiated polymerization and curing processes. For convenience, much of the discussion which follows centers on free radicals as a particularly significant reactive species. Such discussion, however, is not to be construed as limiting either the spirit or scope of the present invention.

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Polymers long have served essential needs in society. For many years, these needs were filled by natural polymers. More recently, synthetic polymers have played an increasingly greater role, particularly since the beginning of the 20th century. Especially useful polymers are those prepared by an addition polymerization mechanism, i.e., free radical chain polymerization of unsaturated monomers, and include, by way of example only, coatings and adhesives. In fact, the majority of commercially significant processes is based on free-radical chemistry. That is, chain polymerization

is initiated by a reactive species which often is a free radical. The source of the free radicals is termed an initiator or photoinitiator.

5 Improvements in free radical chain polymerization have focused both on the polymer being produced and the photoinitiator. Whether a particular unsaturated monomer can be converted to a polymer requires structural, thermodynamic, and kinetic feasibility. Even when
10 all three exist, kinetic feasibility is achieved in many cases only with a specific type of photoinitiator. Moreover, the photoinitiator can have a significant effect on reaction rate which, in turn, may determine the commercial success or failure of a particular polymerization process or product.

15 A free radical-generating photoinitiator may generate free radicals in several different ways. For example, the thermal, homolytic dissociation of an initiator typically directly yields two free radicals per initiator molecule. A photoinitiator, i.e., an initiator which absorbs light energy, may produce free radicals by either of two pathways:

20 (1) the photoinitiator undergoes excitation by energy absorption with subsequent decomposition into one or more radicals; or

25 (2) the photoinitiator undergoes excitation and the excited species interacts with a second compound (by either energy transfer or a redox reaction) to form free radicals from the latter and/or former compound(s).

30 While any free radical chain polymerization process should avoid the presence of species which may prematurely terminate the polymerization reaction, prior photoinitiators present special problems. For example, absorption of the light by the reaction medium may limit the amount of energy available for absorption by the photoinitiator. Also, the often competitive and complex kinetics involved may have an adverse effect on the reaction
35 rate. Moreover, commercially available radiation sources,

such as medium and high pressure mercury and xenon lamps, emit over a wide wavelength range, thus producing individual emission bands of relatively low intensity. Most photoinitiators only absorb over a small portion of the emission spectra and, as a consequence, most of the lamps' radiation remains unused. In addition, most known photoinitiators have only moderate quantum yields (generally less than 0.4) at these wavelengths, indicating that the conversion of light radiation to radical formation could be more efficient. Thus, there are continuing opportunities for improvements in free radical polymerization photoinitiators.

Summary of the Invention

The present invention addresses some of the difficulties and problems discussed above by the discovery of an efficient method for utilizing radiation. Hence, the present invention comprehends a method of generating a reactive species which includes providing a wavelength-specific sensitizer in association with a reactive species-generating photoinitiator and irradiating the wavelength-specific sensitizer. Such method involves effectively tuning the energy-absorbing entity, referred to herein as a polymolecular photoreactor, to efficiently utilize an emitted band of radiation. The wavelength-specific sensitizer effectively absorbs photons and efficiently transfers the absorbed energy to the photoinitiator which, in turn, generates a reactive species. The wavelength-specific sensitizer is adapted to have an absorption peak generally corresponding to a maximum emission band of the radiation source.

The association of a wavelength-specific sensitizer with a reactive species-generating photoinitiator results in a structure referred to herein for convenience as a polymolecular photoreactor. Thus, the method of the present invention may be described as a method of generating a reactive species which involves exposing a polymolecular

photoreactor to radiation, in which the polymolecular photoreactor includes a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator

5 The radiation to which the polymolecular photoreactor is exposed generally will have a wavelength of from about 4 to about 1,000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation, visible radiation, and near
10 infrared radiation. Desirably, the radiation will have a wavelength of from about 100 to about 900 nanometers. More desirably, the radiation will be ultraviolet radiation. e.g., ultraviolet radiation having a wavelength of from about 100 to about 375 nanometers. The radiation desirably will be
15 incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

In its simplest form, the polymolecular photoreactor consists of a single wavelength-specific sensitizer associated with a single reactive species-generating photoinitiator. In this instance, the photoreactor will be a
20 bimolecular photoreactor. However, the photoreactor may include more than one wavelength-specific sensitizer and/or more than one reactive species-generating photoinitiator. When the polymolecular photoreactor is a bimolecular or trimolecular photoreactor and the radiation to which it will be
25 exposed is ultraviolet radiation, the bimolecular or trimolecular photoreactor desirably will contain a benzoyl moiety and a moiety which is either a phthalic acid derivative or a phenyl-substituted aliphatic ketone derivative.

The present invention also comprehends a method
30 of polymerizing an unsaturated monomer by exposing the unsaturated monomer to radiation in the presence of the efficacious polymolecular photoreactor described above. When an unsaturated oligomer/monomer mixture is employed in place of the unsaturated monomer, curing is accomplished.
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Brief Description of the Drawings

FIG. 1 is a diagrammatic representation of the excimer lamp employed in the examples.

5 FIG. 2 is a series of plots of control photoinitiator and polymolecular photoreactor concentration in an adhesive versus through-cure times (radiation exposure times for complete curing) for two control photoinitiators and four polymolecular photoreactors of the present invention.

10 FIG. 3 consists of plots of through-cure times for a control photoinitiator and a polymolecular photoreactor of the present invention at a constant concentration in an adhesive versus film thickness.

Detailed Description of the Invention

15 The term "polymerization" is used herein to mean the combining, e.g. covalent bonding, of large numbers of smaller molecules, such as monomers, to form very large molecules, i.e., macromolecules or polymers. The monomers may be combined to form only linear macromolecules or they
20 may be combined to form three-dimensional macromolecules, commonly referred to as crosslinked polymers.

 As used herein, the term "curing" means the polymerization of functional oligomers and monomers, or even polymers, into a crosslinked polymer network. Thus,
25 curing is the polymerization of unsaturated monomers or oligomers in the presence of crosslinking agents.

 The terms "unsaturated monomer," "functional oligomer," and "crosslinking agent" are used herein with their usual meanings and are well understood by those having
30 ordinary skill in the art. The singular form of each is intended to include both the singular and the plural, i.e., one or more of each respective material.

 The term "unsaturated polymerizable material" is meant to include any unsaturated material capable of
35 undergoing polymerization. The term encompasses unsaturated

monomers, oligomers, and crosslinking agents. Again, the singular form of the term is intended to include both the singular and the plural.

5 The term "wavelength-specific sensitizer" is used herein to mean that the sensitizer is adapted to have an absorption wavelength band generally corresponding to an emission peak of the radiation. Either or both of the sensitizer and the radiation may have more than one absorption wavelength band and emission peak, respectively. In the event
10 both the sensitizer and the radiation have more than one absorption wavelength band and emission peak, respectively, the general correspondence just described need not be limited to a single absorption wavelength band and a single emission peak.

15 The term "quantum yield" is used herein to indicate the efficiency of a photochemical process. More particularly quantum yield is a measure of the probability that a particular molecule will absorb a quantum of light during its interaction with a photon. The term expresses the number of
20 photochemical events per photon absorbed. Thus, quantum yields may vary from zero (no absorption) to 1.

 The term "reactive species" is used herein to mean any chemically reactive species including, but not limited to, free-radicals, cations, anions, nitrenes, and carbenes.

25 The term "associated" as used herein is meant to include any means which results in the wavelength-specific sensitizer and the reactive species-generating photoinitiator being in sufficiently close proximity to each other to permit the transfer of energy absorbed by the sensitizer to the
30 photoinitiator. For example, the wavelength-specific sensitizer and the reactive species-generating photoinitiator may be bonded to each other or to a spacer molecule as described hereinafter by covalent, hydrogen, van der Waals, or ionic bonds. Alternatively, the sensitizer and the photoinitiator may
35 be physically admixed.

5 The method of the present invention involves generating a reactive species by exposing a polymolecular photoreactor to radiation in which the polymolecular photoreactor includes a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator. In other words, the method involves providing a wavelength-specific sensitizer in association with a reactive species-generating photoinitiator and irradiating the wavelength-specific sensitizer. The sensitizer absorbs photons having a specific wavelength and transfers the absorbed energy to the photoinitiator which, in turn, generates a reactive species. However, the efficiency with which a reactive species is generated is significantly greater than that experienced with the reactive species-generating photoinitiator alone. For example, the polymolecular photoreactor desirably will have a quantum yield greater than about 0.5. More desirably, the quantum yield of the polymolecular photoreactor will be greater than about 0.6. Even more desirably, the quantum yield of the polymolecular photoreactor will be greater than about 0.7. Still more desirably, the quantum yield of the polymolecular photoreactor will be greater than about 0.8; with the most desirable quantum yield being greater than about 0.9.

25 As stated above, the polymolecular photoreactor of the present invention includes a wavelength-specific sensitizer in association with a reactive species-generating photoinitiator. Any wavelength-specific sensitizer known to those having ordinary skill in the art may be used in the present invention. Similarly, any reactive species-generating photoinitiator may be used which generates the desired reactive species. Examples of reactive species include, but are not limited to, free radicals, carbenes, nitrenes, cations, and anions. Illustrated below are examples of several of such species.

Examples of carbenes include, for example, methylene or carbene, dichlorocarbene, diphenylcarbene, alkylcarbonylcarbenes, siloxycarbenes, and dicarbenes. Examples of nitrenes include, also by way of example, nitrene, alkyl nitrenes, and aryl nitrenes. Cations (sometimes referred to as carbocations or carbonium ions) include, by way of illustration, primary, secondary, and tertiary alkyl carbocations, such as methyl cation, ethyl cation, propyl cation, *t*-butyl cation, *t*-pentyl cation, *t*-hexyl cation; allylic cations; benzylic cations; aryl cations, such as triphenyl cation; cyclopropylmethyl cations; methoxymethyl cation; triarylsulphonium cations; and acyl cations. Cations also include those formed from various metal salts, such as tetra-*n*-butylammonium tetrahaloaurate(III) salts; sodium tetrachloroaurate(III); vanadium tetrachloride; and silver, copper(I) and (II), and thallium(I) triflates. Examples of anions (sometimes referred to as carbanions) include, by way of example, alkyl anions, such as ethyl anion, *n*-propyl anion, isobutyl anion, and neopentyl anion; cycloalkyl anions, such as cyclopropyl anion, cyclobutyl anion, and cyclopentyl anion; allylic anions; benzylic anions; aryl anions; and sulfur- or phosphorus-containing alkyl anions. Finally, examples of organometallic photoinitiators include titanocenes, fluorinated diaryltitanocenes, iron arene complexes, manganese decacarbonyl, and methylcyclopentadienyl manganese tricarbonyl. Organometallic photoinitiators generally produce free radicals or cations.

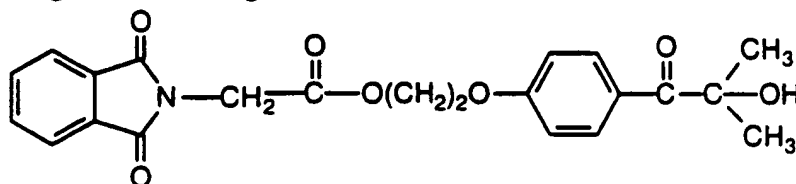
The types of reactions that various reactive species enter into include, but are not limited to, addition reactions, including polymerization reactions; abstraction reactions; rearrangement reactions; elimination reactions, including decarboxylation reactions; oxidation-reduction (redox) reactions; substitution reactions; and conjugation/deconjugation reactions.

With regard to the free radical-generating photoinitiators, these photoinitiators may be any of the photoinitiators known to those having ordinary skill in the art. The largest group of photoinitiators are carbonyl compounds, such as ketones, especially α -aromatic ketones. Examples of α -aromatic ketone photoinitiators include, by way of illustration only, benzophenones; xanthenes and thioxanthenes; α -ketocoumarins; benzils; α -alkoxydeoxybenzoins; benzil ketals or α, α -dialkoxydeoxybenzoins; benzoyldialkylphosphonates; acetophenones, such as α -hydroxycyclohexyl phenyl ketone, α, α -dimethyl- α -hydroxyacetophenone, α, α -dimethyl- α -morpholino-4-methylthioacetophenone, α -ethyl- α -benzyl- α -dimethylaminoacetophenone, α -ethyl- α -benzyl- α -dimethylamino-4-morpholinoacetophenone, α -ethyl- α -benzyl- α -dimethylamino-3,4-dimethoxyacetophenone, α -ethyl- α -benzyl- α -dimethylamino-4-methoxyacetophenone, α -ethyl- α -benzyl- α -dimethylamino-4-dimethylaminoacetophenone, α -ethyl- α -benzyl- α -dimethylamino-4-methylacetophenone, α -ethyl- α -(2-propenyl)- α -dimethylamino-4-morpholinoacetophenone, α, α -bis(2-propenyl)- α -dimethylamino-4-morpholinoacetophenone, α -methyl- α -benzyl- α -dimethylamino-4-morpholinoacetophenone, and α -methyl- α -(2-propenyl)- α -dimethylamino-4-morpholinoacetophenone; α, α -dialkoxyacetophenones; α -hydroxyalkylphenones; O-acyl α -oximino ketones; acylphosphine oxides; fluorenones, such as fluorenone, 2-*t*-butylperoxycarbonyl-9-fluorenone, 4-*t*-butylperoxycarbonyl-nitro-9-fluorenone, and 2,7-di-*t*-butylperoxycarbonyl-9-fluorenone; and α - and β -naphthyl carbonyl compounds. Other free radical-generating photoinitiators include, by way of illustration, triarylsilyl peroxides, such as triarylsilyl *t*-butyl peroxides; acylsilanes; and some organometallic compounds. The free radical-generating initiator desirably will be an acetophenone.

The other component of the polymolecular photoreactor is a wavelength-specific sensitizer. Such sensitizer generally may be any compound which, when associated with the reactive species-generating photoinitiator, absorbs photons having a specific wavelength and transfers the absorbed energy to the photoinitiator. As a practical matter, two classes of compounds are known to be useful as wavelength-specific sensitizers, namely, phthalic acid derivatives and phenyl-substituted aliphatic ketones. A particularly useful example of each class is phthaloylglycine and 4-(4-hydroxyphenyl)butan-2-one, respectively.

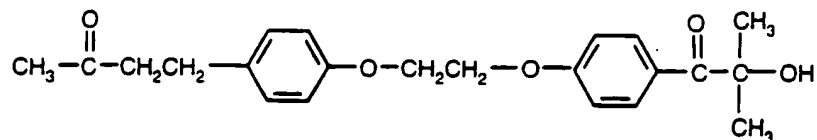
As stated above, the polymolecular photoreactor of the present invention is comprised of a wavelength-specific sensitizer in association with a reactive species-generating photoinitiator. The sensitizer may be in a simple mixture with the photoinitiator, or it may be bonded to the photoinitiator. For example, the sensitizer may be bonded to the photoinitiator by covalent, hydrogen, van der Waals, or ionic bonds.

Desirably, the sensitizer is covalently bonded to the photoinitiator. Desirably, the reactive species-generating photoinitiator of the present invention is 2-[p-(2-methylactoyl)phenoxy]ethyl 1,3-dioxo-2-isoindolineacetate, having the following structure:

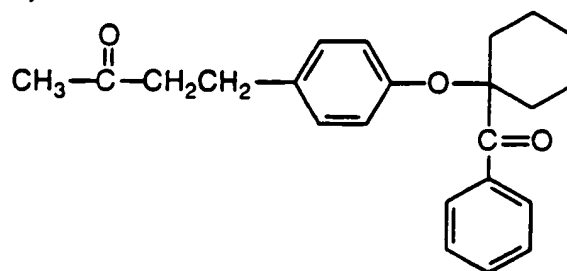


In another embodiment, the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator desirably is 2-hydroxy-2-methyl-4'-[2-[p-(3-oxobutyl)phenoxy]ethoxy]propiophenone, having the following structure:

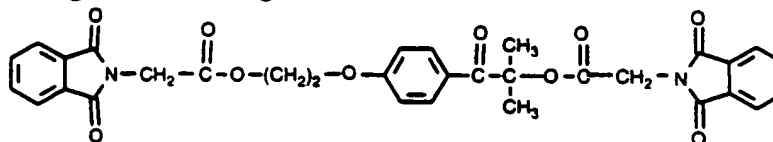
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5 In yet another embodiment, the wavelength-specific sensitizer bonded to the reactive species-generating initiator desirably is 4-[p-[(4-benzoylcyclohexyl)oxy]phenyl]-2-butanone, having the following structure:



10 In still another embodiment, the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator desirably is 1,3-dioxo-2-isoinolineacetic acid diester with 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone, having the following structure:



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20 As noted earlier, the wavelength-specific sensitizer is adapted to have an absorption wavelength band generally corresponding to an emission peak of the radiation. In addition, the wavelength-specific sensitizer will have a high intensity of absorption. For example, the wavelength-specific sensitizer may have a molar extinction coefficient greater than about 5,000 liters per mole per cm ($\text{l mole}^{-1} \text{cm}^{-1}$) at an absorption maximum. As another example, the wavelength-specific sensitizer may have a molar extinction coefficient

(absorptivity) greater than about $10,000 \text{ l mole}^{-1} \text{ cm}^{-1}$. As a further example, the wavelength-specific sensitizer will have a molar extinction coefficient greater than about $20,000 \text{ l mole}^{-1} \text{ cm}^{-1}$.

5 The absorption characteristics of the wavelength-specific sensitizer are not limited to a single wavelength band. Many compounds exhibit more than one absorption wavelength band. Consequently, a wavelength-specific sensitizer may be adapted to absorb two or more wavelength bands of radiation.
10 Alternatively, two or more wavelength-specific sensitizers may be associated with a reactive species-generating photoinitiator. Such two or more wavelength-specific sensitizers may absorb the same wavelength band or they may absorb two or more different wavelength bands of radiation.

15 In the embodiment where the wavelength-specific sensitizer is bound to the reactive species-generating photoinitiator, any suitable method that is known in the art may be used to bond the sensitizer to the photoinitiator. The choice of such method will depend on the functional groups
20 present in the sensitizer and photoinitiator and is readily made by those having ordinary skill in the art. Such bonding may be accomplished by means of functional groups already present in the molecules to be bonded, by converting one or more functional groups to other functional groups, or through one
25 or more spacer molecules. The term "spacer molecule" is used herein to mean any molecule which aids in the bonding process. For example, a spacer molecule may assist in the bonding reaction by relieving steric hindrance. Alternatively, a spacer molecule may allow use of more reactive or more
30 appropriate functional groups, depending upon the functional groups present in the sensitizer and photoinitiator. It is contemplated that a spacer molecule may aid in the transfer of energy from the sensitizer to the photoinitiator, by either allowing a more favorable conformation or providing a more
35 favorable energy transfer pathway.

Exposing the polymolecular photoreactor to radiation results in the generation of a reactive species. Thus, the polymolecular photoreactor may be employed in any situation where reactive species are required, such as for the polymerization of an unsaturated monomer and the curing of an unsaturated oligomer/monomer mixture. The unsaturated monomers and oligomers may be any of those known to one having ordinary skill in the art. In addition, the polymerization and curing media also may contain other materials as desired, such as pigments, extenders, amine synergists, and such other additives as are well known to those having ordinary skill in the art.

By way of illustration only, examples of unsaturated monomers and oligomers include ethylene: propylene: vinyl chloride: isobutylene: styrene: isoprene: acrylonitrile: acrylic acid: methacrylic acid: ethyl acrylate: methyl methacrylate: vinyl acrylate: allyl methacrylate: tripropylene glycol diacrylate: trimethylol propane ethoxylate acrylate: epoxy acrylates, such as the reaction product of a bisphenol A epoxide with acrylic acid; polyester acrylates, such as the reaction product of acrylic acid with an adipic acid/hexanediol-based polyester: urethane acrylates, such as the reaction product of hydroxypropyl acrylate with diphenylmethane-4,4'-diisocyanate: and polybutadiene diacrylate oligomer.

As already noted, the radiation to which the polymolecular photoreactor is exposed generally will have a wavelength of from about 4 to about 1,000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation: visible radiation: and near infrared radiation. Desirably, the radiation will have a wavelength of from about 100 to about 900 nanometers. More desirably, the radiation will have a wavelength of from about 100 to 700 nanometers.

Desirably, when the reactive species-generating photoinitiator is an organic compound, the radiation will be ultraviolet radiation having a wavelength of from about 4 to about 400 nanometers. More desirably, the radiation will have a wavelength of from about 100 to about 375 nanometers, and even more desirably will have a wavelength of from 200 to about 370 nanometers. For example, the radiation may have a wavelength of from about 222 to about 308 nanometers. The radiation desirably will be incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp.

When the wavelength-specific sensitizer is an organometallic compound, the radiation desirably will have a wavelength of from about 4 to about 1,000 nanometers. More desirably, the radiation will have a wavelength of from about 700 to about 900 nanometers. Even more desirably, the radiation will have a wavelength of from about 785 to about 825 nanometers. Most desirably, the radiation will have a wavelength of approximately 800 nanometers.

Dielectric barrier discharge excimer lamps (also referred to hereinafter as "excimer lamp") are described, for example, by U. Kogelschatz, "Silent discharges for the generation of ultraviolet and vacuum ultraviolet excimer radiation." *Pure & Appl. Chem.*, 62, No. 9. pp. 1667-1674 (1990); and E. Eliasson and U. Kogelschatz, "UV Excimer Radiation from Dielectric- Barrier Discharges." *Appl. Phys. B*, 46, pp. 299-303 (1988). Excimer lamps were developed by ABB Infocom Ltd., Lenzburg, Switzerland, and at the present time are available from Heraeus Noblelight GmbH, Kleinostheim, Germany.

The excimer lamp emits incoherent, pulsed ultraviolet radiation. Such radiation has a relatively narrow bandwidth, i.e., the half width is of the order of approximately 5 to 100 nanometers. Desirably, the radiation will have a half width of the order of approximately 5 to 50 nanometers, and more desirably will have a half width of the order of 5 to 25

nanometers. Most desirably, the half width will be of the order of approximately 5 to 15 nanometers.

5 The ultraviolet radiation emitted from an excimer lamp can be emitted in a plurality of wavelengths, wherein one or more of the wavelengths within the band are emitted at a maximum intensity. Accordingly, a plot of the wavelengths in the band against the intensity for each wavelength in the band produces a bell curve. The "half width" of the range of ultraviolet radiation emitted by an excimer lamp is defined as
10 the width of the bell curve at 50% of the maximum height of the bell curve.

The emitted radiation of an excimer lamp is incoherent and pulsed, the frequency of the pulses being dependent upon the frequency of the alternating current power supply which typically is in the range of from about 20 to about 300 kHz. An excimer lamp typically is identified or referred to by the wavelength at which the maximum intensity of the radiation occurs, which convention is followed throughout this specification and the claims. Thus, in
15 comparison with most other commercially useful sources of ultraviolet radiation which typically emit over the entire ultraviolet spectrum and even into the visible region, excimer lamp radiation is essentially monochromatic.

Excimers are unstable excited-state molecular complexes which occur only under extreme conditions, such as those temporarily existing in special types of gas discharge. Typical examples are the molecular bonds between two rare gaseous atoms or between a rare gas atom and a halogen atom. Excimer complexes dissociate within less than a microsecond and, while they are dissociating, release their binding energy in the form of ultraviolet radiation. The dielectric barrier excimers in general emit in the range of from about 125 nm to about 500 nm, depending upon the excimer gas mixture.

Therefore, the present invention provides a
35 method for generating a reactive species by exposing a

polymolecular photoreactor to radiation in which the polymolecular photoreactor includes a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator. Also, as stated above, the polymolecular photoreactor may be employed in any situation where reactive species are required, such as for the polymerization of an unsaturated monomer and the curing of an unsaturated oligomer/monomer mixture.

More particularly, the present invention also provides a method of polymerizing an unsaturated polymerizable material, comprising admixing the polymolecular photoreactor of the present invention with unsaturated polymerizable material, and irradiating the admixture. Desirably, the admixture is irradiated with radiation having a wavelength of from about 4 to about 1000 nanometers. The unsaturated polymerizable material, polymolecular photoreactor, and radiation that may be used in the method of polymerizing an unsaturated polymerizable material are fully described above. In one embodiment, the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

The present invention further provides an adhesive composition comprising the polymolecular photoreactor of the present invention, and an unsaturated polymerizable material that is curable upon exposure to radiation. Similarly, the present invention also provides a laminated structure comprising at least two layers bonded together with the adhesive composition of the present invention, in which at least one layer is a cellulosic or polyolefin nonwoven web or film, and wherein the adhesive composition has been cured by exposure to radiation. The present invention also provides a method of laminating a structure comprising at least two layers, in which at least one layer is a cellulosic or polyolefin nonwoven web or film, with the adhesive composition of the present invention between said

layers, by irradiating the adhesive composition to cure the adhesive composition. The unsaturated polymerizable material, polymolecular photoreactor, and radiation used in this embodiment are fully described above.

5 The present invention also provides a polymer-coated fiber produced by coating a fiber with a composition comprising an admixture of unsaturated polymerizable material and the polymolecular photoreactor of the present invention, and irradiating the coating on the fiber with an
10 amount of radiation sufficient to cure the composition. In one embodiment, the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture. The present invention also provides a method of coating a fiber comprising
15 coating a fiber with a composition comprising an admixture of unsaturated polymerizable material and the polymolecular photoreactor of the present invention, and irradiating the coating on the fiber with an amount of radiation sufficient to
20 cure the composition. In one embodiment, the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture. The unsaturated polymerizable material, polymolecular photoreactor, and radiation used in this
 embodiment are fully described above.

 The present invention further provides a polymer-coated web, produced by coating a web with a composition
25 comprising an admixture of unsaturated polymerizable material and the polymolecular photoreactor of the present invention, and irradiating the coating on the web with an amount of radiation sufficient to cure the composition. The
30 present invention also provides a method of coating a web, comprising coating a web with a composition comprising an admixture of unsaturated polymerizable material and the polymolecular photoreactor of the present invention, and
 irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

5 It is to be understood that the polymerizable material admixed with the polymolecular photoreactor of the present invention is to be admixed by any means known in the art, and that the mixture will be irradiated with an amount of radiation sufficient to polymerize the material. The amount of radiation sufficient to polymerize the material is readily determinable by one of ordinary skill in the art, and depends upon the identity and amount of the polymerizable material, the intensity and wavelength of the radiation, and the duration of the exposure to the radiation.

10 It is also to be understood that the polymer coating on a web or fiber may be any thickness desired, as per the thickness of the admixture applied thereto, so long as the admixture sufficiently polymerizes upon exposure to radiation. Any method known in the art may be used to coat a web or fiber with the admixture of the present invention.

15 The term "fiber" as used herein denotes a threadlike structure. The fibers used in the present invention may be any fibers known in the art. The term "web" or "nonwoven web" are used interchangeably to denote a web-like matter comprised of one or more overlapping or interconnected fibers in a nonwoven manner. It is to be understood that any nonwoven fibers known in the art may be used in the present invention.

25 With respect to the laminated structures of the present invention, it is to be understood that any layers may be used in the present invention, on the condition that at least one of the layers allows sufficient radiation to penetrate through the layer to enable the admixture to polymerize sufficiently. Accordingly, any cellulosic or polyolefin nonwoven web or film known in the art may be used as one of the layers so long as they allow radiation to pass through. Again, the amount of radiation sufficient to polymerize the admixture is readily determinable by one of ordinary skill in the art, and depends upon the identity and amount of photoreactor composition, the

30

35

identity and amount of polymerizable material, the thickness of the admixture, the identity and thickness of the layer, the intensity and wavelength of the radiation, and duration of exposure to the radiation.

5 The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention. In the examples, all parts are by weight, unless stated otherwise.

10

Example 1

This example describes the preparation of the bimolecular photoreactor, 2[p-(2-methylactoyl)phenoxy]ethyl 1,3-dioxo-2-isoinolineacetate.

15 A 250 ml, three-necked, round-bottomed flask was fitted with a Dean and Stark apparatus with condenser and two glass stoppers. The flask was charged with 20.5 g (0.1 mole) of phthaloylglycine (Aldrich Chemical Company, Milwaukee, Wisconsin), 24.6 g (0.1 mole) of Darcur® 2959
20 (α,α -dimethyl- α -hydroxy-4-(2-hydroxyethoxy)acetophenone, Ciba-Geigy Corporation, Hawthorne, New York), 100 ml of benzene (Aldrich), and 0.4 g of *p*-toluenesulfonic acid (Aldrich). The resulting mixture was heated at reflux temperature for three hours, after which time 1.8 ml (0.1
25 mole) of water was collected in the Dean and Stark apparatus. The solvent was removed to give 43.1 g of white powder. The powder was recrystallized from 30 volume percent ethyl acetate in hexane (Fisher Scientific, Pittsburgh, Pennsylvania) to give 40.2 g (93 percent yield) of a white crystalline powder
30 having a melting point of 153-4°C.

The expected structure was verified by infrared and nuclear magnetic resonance analyses. The infrared spectrum of the powder was obtained as a Nujol mull and showed absorption maxima at 3440, 1760, 1680, and

1600 cm^{-1} . The nuclear magnetic resonance data for the powder were as follows:

5 ^1H NMR (CDCl_3): 1.64 (s), 4.25 (m), 4.49 (m), 6.92 (m),
7.25 (m), 7.86 (m), 7.98 (m), 8.06 (m)
ppm.

Example 2

10 This example describes the preparation of the
bimolecular photoreactor, 2-hydroxy-2-methyl-4'-[2-[*p*-(3-oxobutyl)phenoxy]ethoxy]propiofenone. The preparation
was carried out in two steps.

15 A 100-ml round-bottomed flask was charged with
24.6 g (0.1 mole) of Darcu[®] 2959, 20 ml of toluene
(Aldrich), 11.9 g (0.1 mole) of thionyl chloride (Aldrich), and
0.5 ml of pyridine (Aldrich). The flask was fitted with a
condenser and the reaction mixture was heated at reflux
temperature for two hours. The solvent was removed by
distillation at reduced pressure (0.1 Torr) to yield a colorless
20 solid which was used without purification.

To a 250-ml, three-necked, round-bottomed flask
fitted with a condenser and a magnetic stirring bar was added
17.6 g (0.1 mole) of 4-(4-hydroxyphenyl)butan-2-one
(Aldrich), the chloro-substituted Darcu[®] 2959 (α,α -
25 dimethyl- α -hydroxy-4-(2-chloroethoxy)acetophenone)
prepared as described above, 1.0 ml of pyridine, and 100 ml
of anhydrous tetrahydrofuran (Aldrich). The mixture was
heated at reflux temperature for three hours and the solvent
then was partially (about 60 volume percent) removed under
30 reduced pressure. The remaining mixture was poured into ice
water and extracted with two 50-ml aliquots of diethyl ether
(Aldrich). The ether extracts were combined and dried over
anhydrous magnesium sulfate. Removal of the solvent left
39.1 g of a white solid. Recrystallization of the solid as

described in Example 1 gave 36.7 g (91 percent yield) of a white crystalline powder having a melting point of 142-3°C.

The expected structure was verified by infrared and nuclear magnetic resonance analyses. The infrared spectrum of the powder was obtained as a Nujol mull and showed absorption maxima at 3460, 1740, 1700, 1620, and 1600 cm^{-1} . The nuclear magnetic resonance data for the powder were as follows:

^1H NMR (CDCl_3): 1.62 (s), 4.2 (m), 4.5 (m), 6.9 (m) ppm.

Example 3

This example describes the preparation of the bimolecular photoreactor, [*p* - [(4-benzoylcyclohexyl)oxy]phenyl]-2-butanone.

To a 250-ml, two-necked, round-bottomed flask fitted with a condenser and a stopper was added 20.4 g (0.1 mole) of Irgacure® 184 (Ciba-Geigy) and 100 ml of anhydrous tetrahydrofuran. The mixture was stirred and cooled to ice/salt bath temperature while flushing the flask with argon. To the resulting solution was added slowly 20.0 g (0.15 mole) of aluminum chloride (Aldrich) over a 40 minute period. The resulting mixture was stirred an additional 20 minutes. To the mixture then was added 17.6 g (0.1 mole) of 4-(4-hydroxyphenyl)butan-2-one. The new mixture was stirred overnight while being allowed to warm to ambient temperature. The reaction mixture then was poured into ice water and extracted with three 50-ml portions of diethyl ether. Removal of the ether gave 34.1 g of a white solid. Recrystallization of the solid from 10 volume percent ethyl acetate in hexane gave 30.2 g (83 percent) of a white crystalline powder having a melting point of 136-8°C.

The expected structure was verified by infrared and nuclear magnetic resonance analyses. The infrared

spectrum of the powder was obtained as a Nujol mull and showed absorption maxima at 1760, 1740, 1620, and 1600 cm^{-1} . The nuclear magnetic resonance data for the powder were as follows:

5

^1H NMR (CDCl_3): 2.10 (s), 2.70 (m), 6.80 (m), 6.92 (m), 8.42 (m) ppm.

Example 4

10

This example describes the preparation of the trimolecular photoreactor, 1,3-dioxo-2-isindolineacetic acid, diester with 2-hydroxy-4'-(2-hydroxyethoxy)2-methylpropiophenone.

15

A 250-ml, two-necked, round-bottomed flask was fitted with a condenser and a Dean and Stark apparatus. The flask was charged with 41.0 g (0.2 mole) of phthaloylglycine, 24.6 g (0.1 mole) of Darcur® 2959, 100 ml of benzene, and 3 ml of concentrated sulfuric acid (Fisher). The mixture was heated at reflux temperature for three hours, after which time 20 3.6 ml (0.2 mole) of water had been collected in the Dean and Stark apparatus. The solvent was removed from the reaction mixture to give 61.8 g of a solid. The material was recrystallized as described in Example 1 to give 57.6 g (93 percent) of product having a melting point of 168-9°C.

25

The expected structure was verified by infrared and nuclear magnetic resonance analyses. The infrared spectrum of the powder was obtained as a Nujol mull and showed absorption maxima at 1760, 1740, 1620, and 1600 cm^{-1} . The nuclear magnetic resonance data for the powder were as follows:

30

^1H NMR (CDCl_3): 1.64 (s), 4.25 (m), 4.49 (m), 6.91 (m), 7.30 (m), 7.84 (m), 7.98 (m), 8.06 (m) ppm.

35

Example 5

This example describes the evaluation of the curing behavior of adhesives containing the polymolecular photoreactors of Examples 1-4, inclusive, upon exposure to ultraviolet radiation from an excimer lamp.

An excimer lamp configured substantially as described by Kozelschatz and Eliasson et al., supra, was employed and is shown diagrammatically in FIG. 1. With reference to FIG. 1, the excimer lamp 100 consisted of three coaxial quartz cylinders and two coaxial electrodes. The outer coaxial quartz cylinder 102 was fused at the ends thereof to a central coaxial quartz cylinder 104 to form an annular discharge space 106. An excimer-forming gas mixture was enclosed in the annular discharge space 106. An inner coaxial quartz cylinder 108 was placed within the central cylinder 104. The inner coaxial electrode 110 consisted of a wire wound around the inner cylinder 108. The outer coaxial electrode 112 consisted of a wire mesh having a plurality of openings 114. The inner coaxial electrode 110 and outer coaxial electrode 112 were connected to a high voltage generator 116. Electrical discharge was maintained by applying an alternating high voltage to the coaxial electrodes 110 and 112. The operating frequency was 40 kHz, the operating voltage 10 kV. Cooling water was passed through the inner coaxial quartz cylinder 108, thereby maintaining the temperature at the outer surface of the lamp at less than about 120°C. The resulting ultraviolet radiation was emitted through the openings 114 as shown by lines 118. The lamp was used as an assembly of four lamps 100 mounted side-by-side in a parallel arrangement.

A standard adhesive mixture was prepared by mixing 90 parts by weight of Genomer® D15OOB Difunctional Polyester Urethane Acrylate (Mader, Biddle Sawyer Corporation, New York, New York) and 9 parts of pentaerythritol triacrylate (Polysciences, Inc., Warrington,

Pennsylvania). The mixture was stirred by means of a magnetic stirring bar for 20 minutes at 80°C.

To aliquots of the standard adhesive mixture were added the compounds of Examples 1-4, respectively. Two control mixtures were prepared using commercially available photoinitiators, Irgacure® 907 (α,α -dimethyl- α -morpholino-4-methylthiophenylacetophenone or 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, Ciba-Geigy) as Control A, and Darcur® 2959 as Control B. In each case, the amount of photoinitiator or photoreactor added was 1 part. Each resulting mixture was stirred thoroughly. A few drops of each mixture were placed on a metal plate (Q-Panel Company, Cleveland, Ohio) and drawn down to a film having a thickness of about 0.6 mil (about 0.015 mm) by means of a draw-down bar (Industry Tech., Oldsmar, Florida). Each film then was exposed to 222 nanometer (nm) ultraviolet radiation emitted by a KrCl* excimer lamp for a period of time sufficient to cure the film (through-cure time).

A film of adhesive was deemed cured completely, i.e., through the entire thickness of the film, when it passed the scratch test; see, e.g., M. Braithwaite et al., "Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints," Vol. IV, SITA Technology Ltd., London, 1991, pp. 11-12. The results are summarized in Table 1.

Table 1
Summary of Through-Cure Times
With Constant Photoreactor Concentration

<u>Photoreactor</u>	<u>Through-Cure Time (Sec.)</u>
Control A	15.0
Control B	12.4
Example 1	2.0
Example 2	3.2
Example 3	4.6
Example 4	2.2

5

Example 6

The procedure of Example 5 was repeated with varying concentrations of photoreactor. The amount of pentaerythritol triacrylate was decreased as required to provide 100 parts of control photoinitiator- or photoreactor-containing adhesive. The results are summarized in Table 2 (the data for a control photoinitiator or photoreactor concentration of 1 percent are from Example 1).

10

15

Table 2
Summary of Through-Cure Times
With Varying Photoreactor Concentrations

<u>Photoreactor</u>	<u>Through-Cure Time (Sec.)</u>			
	<u>1 Percent</u>	<u>2 Percent</u>	<u>3 Percent</u>	<u>4 Percent</u>
Control A	15.0	11.0	8.0	5.0
Control B	12.4	7.4	5.8	4.0
Example 1	2.0	1.4	0.9	0.5
Example 2	3.2	2.6	1.9	1.1
Example 3	4.6	3.9	2.7	2.0
Example 4	2.2	1.6	1.0	0.6

While the data in Tables 1 and 2 clearly demonstrate the remarkable improvements in cure rates which are achieved with the polymolecular photoreactors of the present invention, the data in Table 2 were plotted as photoreactor concentration versus through-cure time. The resulting plots, shown in FIG. 2, dramatically illustrate such remarkable improvements.

Example 7

A series of experiments was carried out as described in Example 5, using only Control B and the polymolecular photoreactor of Example 1 in order to determine the effect of film thickness on through-cure times. In each case, the concentration of control photoinitiator or photoreactor was 4 weight percent. The results are summarized in Table 3 (the data for a film thickness of 0.6 mil are from Table 1).

Table 3
Summary of Through-Cure Times
With Varying Film Thicknesses

<u>Film Thickness</u>		<u>Through-Cure Time (Sec.)</u>	
<u>Mils</u>	<u>mm</u>	<u>Control B</u>	<u>Example 1</u>
0.6	0.015	4.0	0.5
1.0	0.025	6.1	0.8
2.0	0.051	14.2	1.4
3.0	0.076	21.0	2.0

5

Regardless of the film thickness employed, the polymolecular photoreactor of Example 1 clearly provided much faster curing rates. In order to better visualize the extent of improvement and any trends which may be present, the data of Table 3 were plotted as film thickness in mils versus through-cure times. The plots are shown in FIG. 3. While it is evident that film thickness affects through-cure time approximately linearly in each case, the rate of increase with increasing film thickness for the control photoinitiator is much greater than for the polymolecular photoreactor of Example 1.

15

It may be noted that, because of the high molar absorptivity of the polymolecular photoreactors of the present invention, film thickness/cure limitations may be observed with very thick film thicknesses. For example, a 25mil (about 0.64-mm) adhesive film containing the photoreactor of Example 1 remained tacky on the side adjacent to the metal plate supporting the film, even though the upper surface, or top of the film, passed the scratch test.

20

25

Example 8

The procedure of Example 1 was repeated with Control A, Control B, and the photoreactor of Example 1 in order to test the curing behavior of the films upon exposure to

the radiation from another ultraviolet light source. In this case, a 550-watt, wide spectrum emission, Hanovia medium pressure mercury lamp (Hanovia Lamp Co., Newark, New Jersey) was employed in place of the excimer lamp. The distance from the lamp to the sample being irradiated was about 16 inches (about 41 cm). The results are summarized in Table 4.

Table 4
Summary of Results with
Medium Pressure Mercury Lamp

<u>Photoreactor</u>	<u>Through-Cure Time</u>
Control A	60 seconds
Control B	90 seconds
Example 1	15 seconds

The superiority of the polymolecular photoreactors of the present invention over known photoinitiators is clear, even when the radiation is not the essentially monochromatic emission which is characteristic of an excimer lamp. The effective tuning of the polymolecular photoreactor for a specific wavelength band permits the photoreactor to more efficiently utilize any radiation in the emission spectrum of the radiating source corresponding to the "tuned" wavelength band, even though the intensity of such radiation may be much lower than, for example, radiation from a narrow band emitter such as an excimer lamp. In other words, the effectiveness of the polymolecular photoreactor of the present invention is not dependent upon the availability or use of a narrow wavelength band radiation source.

Example 9

Finally, the procedure of Example 5 was repeated using simple mixtures of sensitizer and photoinitiator. Two mixtures were studied. The first (Mixture A) consisted of Control A and phthaloylglycine, each being present at a level in the adhesive of 1 weight percent. The second mixture (Mixture B) consisted of Control B and phthaloylglycine: again, each component was present at a level of 1 weight percent. The results are summarized in Table 5.

Table 5
Summary of Results with Mixtures
of Sensitizer and Photoinitiator

<u>Mixture</u>	<u>Through-Cure Time</u>
A	12.8 seconds
B	10.1 seconds

It will be remembered from Table 1 of Example 5 that the through-cure times for Controls A and B at levels of 1 weight percent were 15.0 and 12.4 seconds, respectively. It likewise will be remembered that the through-cure time for the bimolecular photoreactor of Example 1, also present at a level of 1 weight percent, was 2.0 seconds. Given the fact that each of the components in the mixtures summarized in Table 5 was present at a level of 1 weight percent, it is evident that mixtures of the sensitizers and photoinitiators in these Examples are essentially no more effective than the photoinitiator alone. Thus, the unique results obtained with the polymolecular photoreactors of these Examples were dependent upon the covalent bonding of the sensitizer to the free radical generating photoinitiator. Nevertheless, it is believed that physical mixtures of the sensitizer and photoinitiator are capable of results better than those achievable with photoinitiator alone. It is postulated that such

mixtures may be optimized by improving the blending and/or the amounts of the two components.

5 While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention
10 should be assessed as that of the appended claims and any equivalents thereto.

CLAIMS

1. A method of generating a reactive species,
comprising:
5 providing a wavelength-specific sensitizer in
association with a reactive species-generating photoinitiator;
and
irradiating the wavelength-specific sensitizer.
- 10 2. The method of claim 1, wherein the
wavelength-specific sensitizer is irradiated with radiation
having a wavelength of from about 4 to about 1000
nanometers.
- 15 3. The method of claim 2, wherein the
radiation is ultraviolet radiation.
- 20 4. The method of claim 3, wherein the
ultraviolet radiation is incoherent, pulsed ultraviolet radiation
from a dielectric barrier discharge excimer lamp.
- 25 5. The method of claim 4, wherein the
ultraviolet radiation from the dielectric barrier discharge
excimer lamp has a half width of about 5 to 100 nanometers.
- 30 6. The method of claim 2, wherein the
radiation is infrared radiation.
7. The method of claim 1, wherein the
reactive species generated is a free radical, carbene, nitrene,
anion, or cation.

8. The method of claim 1, wherein the quantum yield of the wavelength-specific sensitizer in association with a reactive species-generating photoinitiator is greater than about 0.6.

5

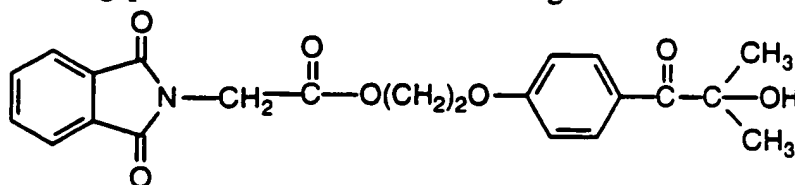
9. The method of claim 3, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

10

10. The method of claim 1, wherein the wavelength-specific sensitizer is covalently bonded to the reactive species-generating photoinitiator.

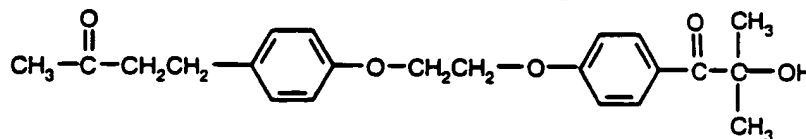
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11. The method of claim 10, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:

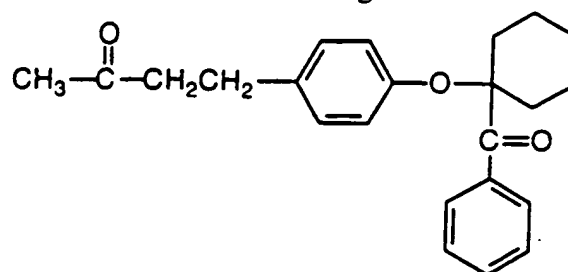


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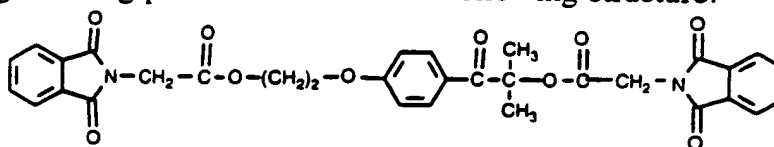
12. The method of claim 10, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



13. The method of claim 10, wherein the wavelength-specific sensitizer bonded to the reactive species-generating initiator has the following structure:



14. The method of claim 10, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



15. A method of polymerizing an unsaturated polymerizable material, comprising:

providing a polymolecular photoreactor comprising a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator;

admixing unsaturated polymerizable material with the polymolecular photoreactor; and

irradiating the unsaturated polymerizable material admixed with the polymolecular photoreactor.

16. The method of Claim 15, wherein the unsaturated polymerizable material admixed with the polymolecular photoreactor is irradiated with radiation having a wavelength of from about 4 to 1000 nanometers.

17. The method of Claim 16, wherein the radiation is ultraviolet radiation.

18. The method of Claim 16, wherein the radiation is infrared radiation.

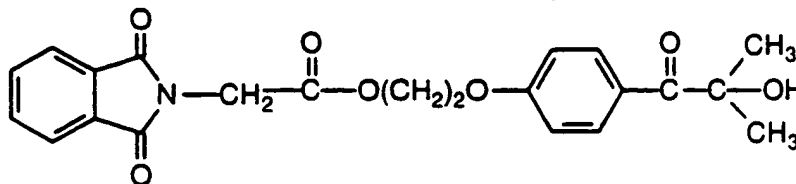
19. The method of Claim 15, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

20. The method of Claim 15, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

21. The method of Claim 15, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

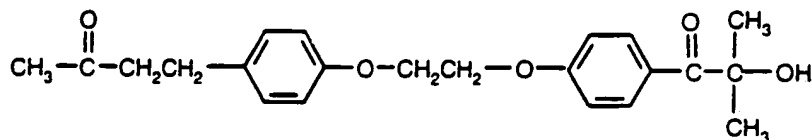
22. The method of Claim 15, wherein the wavelength-specific sensitizer is covalently bonded to the reactive species-generating photoinitiator

23. The method of Claim 22, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



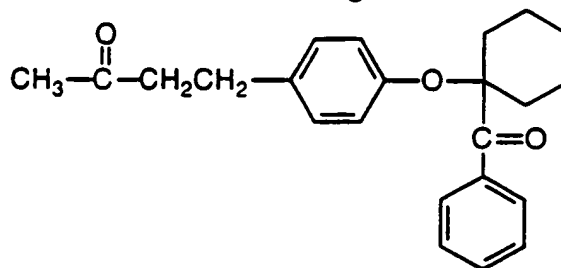
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24. The method of Claim 22, wherein the wavelength-specific sensitizer bonded to the reactive species generating initiator has the following structure:



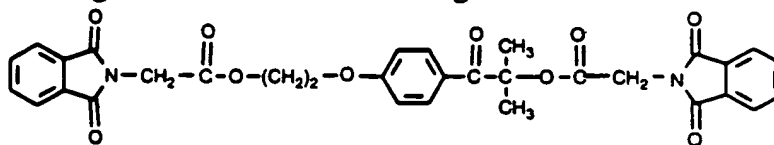
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25. The method of Claim 22, wherein the wavelength-specific sensitizer bonded to the reactive species generating initiator has the following structure:



10

26. The method of Claim 22, wherein the wavelength-specific sensitizer bonded to the reactive species generating initiator has the following structure:



15

27. An adhesive composition comprising a polymolecular photoreactor comprising a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator, and an unsaturated polymerizable material,

20

wherein the composition is curable upon exposure to radiation.

28. The adhesive of Claim 27, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

5

29. The adhesive of Claim 27, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

10

30. A laminated structure, comprising at least two layers bonded together with an adhesive composition, in which at least one layer is a cellulosic or polyolefin nonwoven web or film,

15

wherein the adhesive composition comprises an unsaturated polymerizable material and a polymolecular photoreactor, the polymolecular photoreactor comprising a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator, and

20

wherein the composition has been cured by exposure to radiation.

25

31. The laminated structure of Claim 30, wherein the reactive species-generating photoinitiator when exposed to radiation generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

30

32. The laminated structure of Claim 30, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

33. A method of laminating a structure,
providing a structure comprising at least two
layers, in which at least one layer is a cellulosic or polyolefin
nonwoven web or film, with an adhesive composition between
5 said layers, and

irradiating the adhesive composition to cure the
adhesive composition,

wherein the adhesive composition comprises a
polymolecular photoreactor comprising a wavelength-specific
10 sensitizer associated with a reactive species-generating
photoinitiator, and an unsaturated polymerizable material.

34. The method of Claim 33, wherein the
reactive species-generating photoinitiator when irradiated
15 generates a reactive species that is a free radical, carbene,
nitrene, anion, or cation.

35. The method of Claim 33, wherein the
wavelength-specific sensitizer is a phthalic acid derivative, or a
20 phenyl-substituted aliphatic ketone derivative.

36. A polymer-coated fiber, produced by the
process of:

25 providing a fiber coated with a composition
comprising an admixture of unsaturated polymerizable
material and a polymolecular photoreactor, wherein the
polymolecular photoreactor comprises a wavelength-specific
sensitizer associated with a reactive species-generating
photoinitiator; and

30 irradiating the coating on the fiber with an
amount of radiation sufficient to cure the composition.

37. The polymer-coated fiber of Claim 36,
wherein the unsaturated polymerizable material is an
35 unsaturated oligomer/monomer mixture.

38. The polymer-coated fiber of Claim 36, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

39. The polymer-coated fiber of Claim 36, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

40. A method of coating a fiber, comprising:
providing a fiber coated with a composition comprising an admixture of unsaturated polymerizable material and a polymolecular photoreactor, wherein the polymolecular photoreactor comprises a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator; and

irradiating the coating on the fiber with an amount of radiation sufficient to cure the composition.

41. The method of Claim 40, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

42. The method of Claim 40, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

43. The method of Claim 40, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

44. A polymer-coated web, produced by the process of:

5 providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a polymolecular photoreactor, wherein the polymolecular photoreactor comprises a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator; and

10 irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

45. A method of coating a web, comprising:

15 providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a polymolecular photoreactor, wherein the polymolecular photoreactor comprises a wavelength-specific sensitizer associated with a reactive species-generating photoinitiator; and

20 irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

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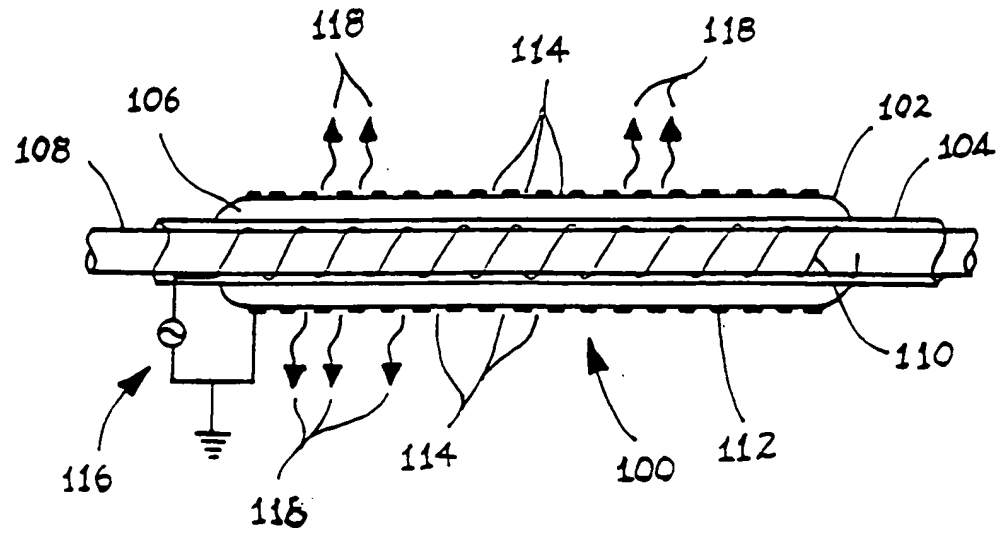


FIG. 1

2/2

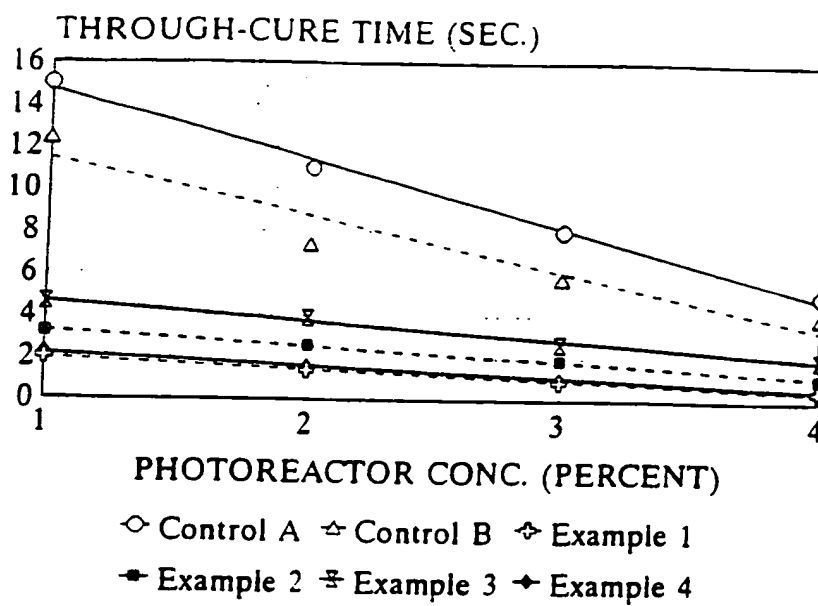


FIG. 2

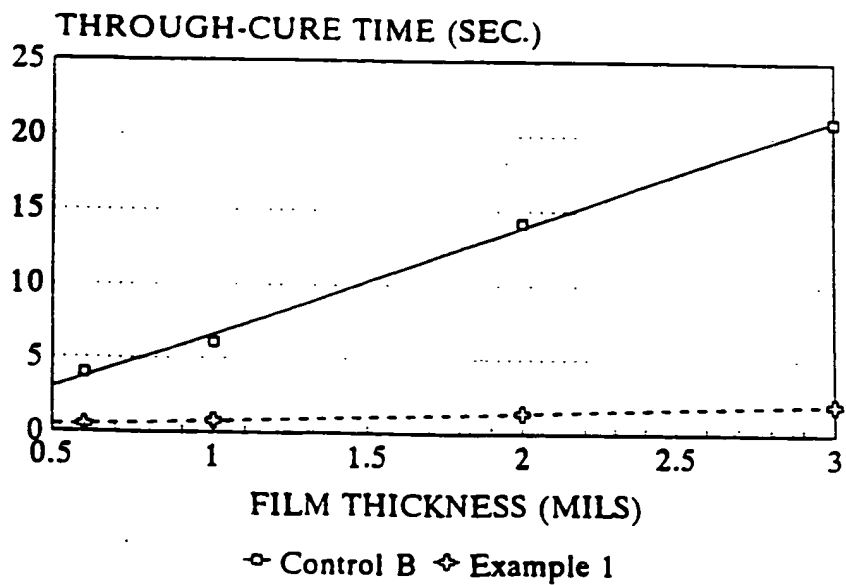


FIG. 3

INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/US 95/07714

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F2/50 C09J4/00 C09D4/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 571 377 (V.D. MC GINNISS) 18 February 1986	
A	EP,A,0 127 574 (CIBA-GEIGY) 5 December 1984	
A	EP,A,0 375 160 (MINNESOTA MINING AND MANUFACTURING CO.) 27 June 1990	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 October 1995

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4571377	18-02-86	NONE	
EP-A-0127574	05-12-84	DE-A- 3466742 JP-A- 59206425	12-11-87 22-11-84
EP-A-0375160	27-06-90	US-A- 4954416 CA-A- 2003569 DE-D- 68921585 DE-T- 68921585 JP-A- 2242803	04-09-90 21-06-90 13-04-95 12-10-95 27-09-90

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1 February 1996 (01.02.96)

(54) Title: METHOD OF GENERATING A REACTIVE SPECIES AND APPLICATIONS THEREFOR

(57) Abstract

A method of generating reactive species which includes exposing a polymolecular photoreactor to radiation, in which the polymolecular photoreactor comprises a wavelength-specific sensitizer associated with a reactive species generating photoinitiator. The sensitizer absorbs energy and transfers the absorbed energy to the photoinitiator which, in turn, generates reactive species. The wavelength-specific sensitizer is adapted to have an absorption wavelength band generally corresponding to an emission peak of the radiation. The radiation to which the polymolecular photoreactor is exposed generally will have a wavelength of from about 4 to about 1,000 nanometers. Thus, the radiation may be ultraviolet radiation, including near ultraviolet and far or vacuum ultraviolet radiation; visible radiation; and near infrared radiation. Desirably, the radiation will have a wavelength of from about 100 to about 900 nanometers. More desirably, in one embodiment, the radiation will have a wavelength of from about 100 to about 375 nanometers, in which case the radiation desirably is incoherent, pulsed ultraviolet radiation from a dielectric barrier discharge excimer lamp. Also described are methods of polymerizing unsaturated monomers and curing an unsaturated oligomer/monomer mixture.

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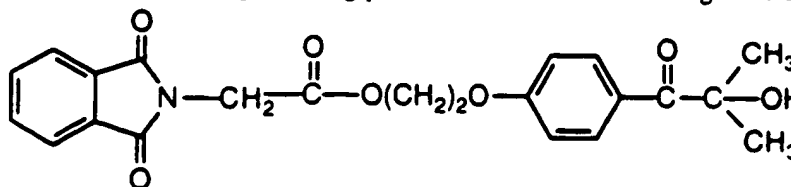
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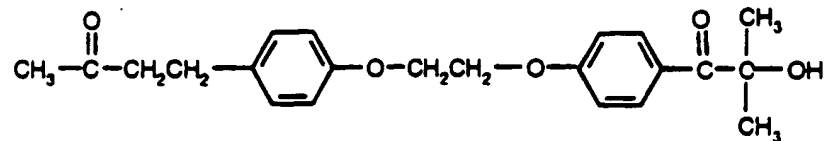
AMENDED CLAIMS

[received by the International Bureau on 22 December 1995 (22.12.95);
original claims 1-45 replaced by amended claims 1-89 (14 pages)]

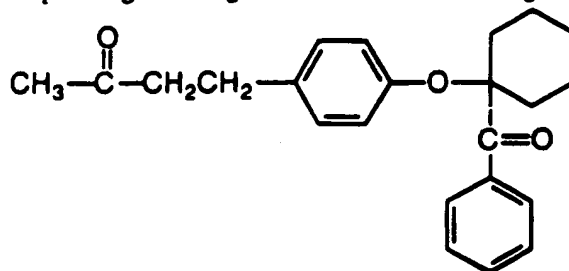
1. A method of generating a reactive species, comprising:
providing a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and
irradiating the wavelength-specific sensitizer.
2. The method of claim 1, wherein the wavelength-specific sensitizer is irradiated with radiation having a wavelength of from about 4 to about 1000 nanometers.
3. The method of claim 1, wherein the wavelength-specific sensitizer covalently bonded to the reactive species-generating photoinitiator has a quantum yield greater than about 0.5.
4. The method of claim 1, wherein the reactive species generated is a free radical, carbene, nitrene, anion, or cation.
5. The method of claim 1, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.
6. The method of claim 1, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.
7. The method of claim 1, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



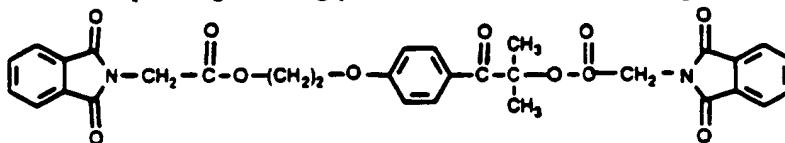
8. The method of claim 1, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



9. The method of claim 1, wherein the wavelength-specific sensitizer bonded to the reactive species-generating initiator has the following structure:



10. The method of claim 1, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has the following structure:



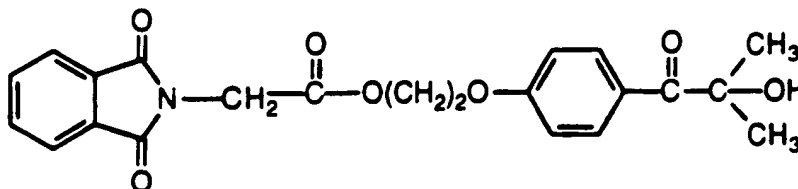
11. A method of generating a reactive species, comprising:
 providing a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, wherein the wavelength-specific sensitizer bonded to the reactive species-generating photoinitiator has a quantum yield greater than about 0.5; and
 irradiating the wavelength-specific sensitizer.

12. The method of claim 11, wherein the wavelength-specific sensitizer is irradiated with radiation having a wavelength of from about 4 to about 1000 nanometers.

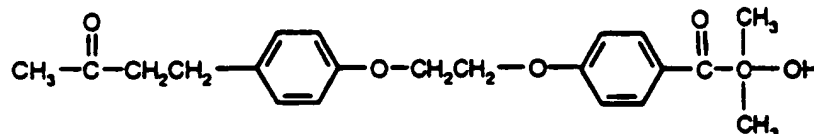
13. The method of claim 11, wherein the reactive species generated is a free radical, carbene, nitrone, anion, or cation.

14. The method of claim 11, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.
15. The method of claim 11, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.
16. A method of polymerizing an unsaturated polymerizable material, comprising:
providing a photoreactor admixed with an unsaturated polymerizable material, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and
irradiating the unsaturated polymerizable material admixed with the photoreactor.
17. The method of Claim 16, wherein the unsaturated polymerizable material admixed with the photoreactor is irradiated with radiation having a wavelength of from about 4 to 1000 nanometers.
18. The method of Claim 16, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.
19. The method of Claim 16, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.
20. The method of Claim 16, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

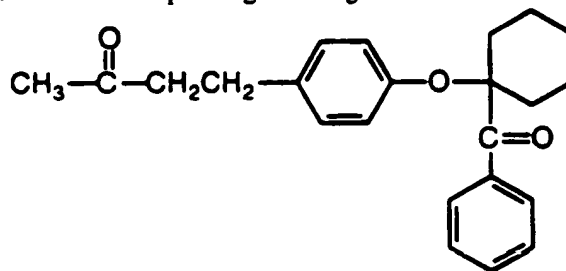
21. The method of Claim 16, wherein the wavelength-specific sensitizer covalently bonded to the reactive species-generating photoinitiator has the following structure:



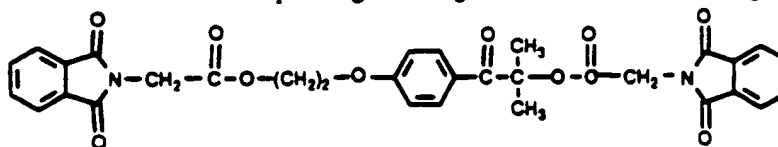
22. The method of Claim 16, wherein the wavelength-specific sensitizer covalently bonded to the reactive species generating initiator has the following structure:



23. The method of Claim 16, wherein the wavelength-specific sensitizer covalently bonded to the reactive species generating initiator has the following structure:



24. The method of Claim 16, wherein the wavelength-specific sensitizer covalently bonded to the reactive species generating initiator has the following structure:



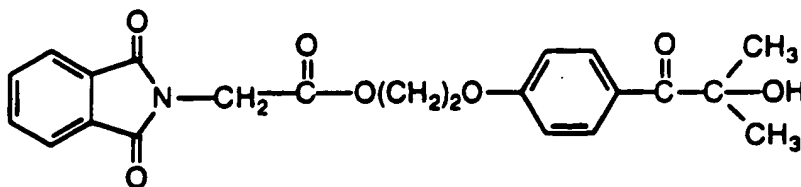
25. The method of Claim 16, wherein the photoreactor has a quantum yield greater than about 0.5.

26. The method of Claim 16, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.
27. A method of polymerizing an unsaturated polymerizable material, comprising:
providing a photoreactor admixed with an unsaturated polymerizable material, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5; and
irradiating the unsaturated polymerizable material admixed with the photoreactor.
28. The method of claim 27, wherein the wavelength-specific sensitizer is irradiated with radiation having a wavelength of from about 4 to about 1000 nanometers.
19. The method of Claim 27, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.
30. The method of claim 27, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.
31. The method of claim 27, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.
32. An adhesive composition comprising a photoreactor admixed with an unsaturated polymerizable material, wherein the composition is curable upon exposure to radiation,
wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum.
33. The adhesive of Claim 32, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

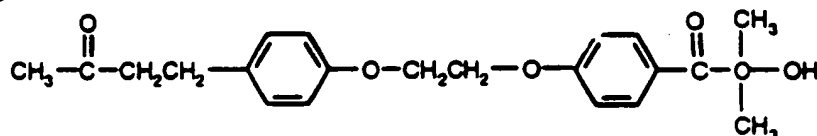
34. The adhesive of Claim 32, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

35. The adhesive of Claim 32, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

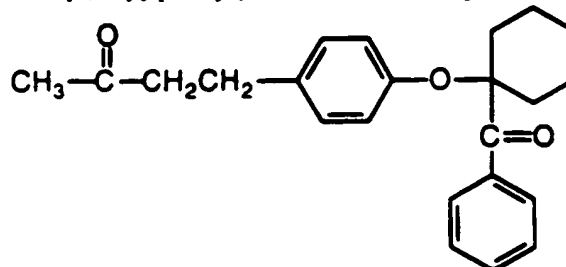
36. The adhesive of Claim 32, wherein the photoreactor is 2-[*p*-(2-methylactoyl)phenoxy]ethyl-1,3-dioxo-2-isoindolineacetate, having the following structure:



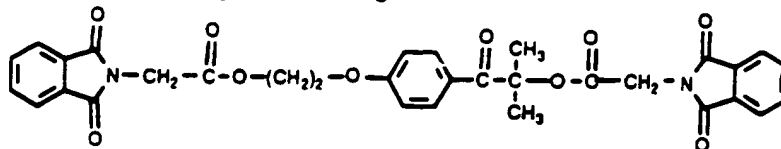
37. The adhesive of Claim 32, wherein the photoreactor is 2-hydroxy-2-methyl-4'-[2-[*p*-(3-oxobutyl)phenoxy]ethoxy]propiophenone, having the following structure:



38. The adhesive of Claim 32, wherein the photoreactor is 4-[*p*-[(4-benzoylcyclohexyl)oxy]-phenyl]-2-butanone, having the following structure:



39. The adhesive of Claim 32, wherein the photoreactor is 1,3-dioxo-2-isoinolineacetic acid, diester with 2-hydroxy-4'- (2-hydroxyethoxy)-2-methylpropiophenone, having the following structure:



40. The adhesive of Claim 32, wherein the photoreactor has a quantum yield greater than about 0.5.

41. A laminated structure, comprising at least two layers bonded together with an adhesive composition, in which at least one layer is a cellulosic or polyolefin nonwoven web or film,

wherein the adhesive composition comprises an unsaturated polymerizable material and a photoreactor, the photoreactor comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and

wherein the composition has been cured by exposure to radiation, and the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum.

42. The laminated structure of Claim 41, wherein the reactive species-generating photoinitiator when exposed to radiation generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

43. The laminated structure of Claim 41, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

44. The laminated structure of Claim 41, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

45. The laminated structure of Claim 41, wherein the photoreactor has a quantum yield greater than about 0.5.

46. A method of laminating a structure, providing a structure comprising at least two layers, in which at least one layer is a cellulosic or polyolefin nonwoven web or film, with an adhesive composition between said layers, and

irradiating the adhesive composition to cure the adhesive composition, wherein the adhesive composition comprises a photoreactor admixed with an unsaturated polymerizable material, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum.

47. The method of Claim 46, wherein the the adhesive composition is irradiated with radiation having a wavelength of from about 4 to about 1000 nanometers.

48. The method of Claim 46, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species selected from the group consisting of a free radical, carbene, nitrene, anion, and cation.

49. The method of Claim 46, wherein the wavelength-specific sensitizer is selected from a group consisting of a moiety which is a phthalic acid derivative, and a moiety which is a phenyl-substituted aliphatic ketone derivative.

50. The method of Claim 46, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

51. The method of of Claim 46 wherein the photoreactor has a quantum yield greater than about 0.5.

52. An adhesive composition comprising a photoreactor admixed with an unsaturated polymerizable material, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, wherein the composition is curable upon exposure to radiation, and the photoreactor has a quantum yield greater than about 0.5.

53. The adhesive of Claim 52, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

54. The adhesive of Claim 52, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

55. The adhesive of Claim 52, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

56. A laminated structure, comprising at least two layers bonded together with an adhesive composition, in which at least one layer is a cellulosic or polyolefin nonwoven web or film,

wherein the adhesive composition comprises an unsaturated polymerizable material and a photoreactor, the photoreactor comprising a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and

wherein the composition has been cured by exposure to radiation and the photoreactor has a quantum yield greater than about 0.5.

57. The laminated structure of Claim 56, wherein the reactive species-generating photoinitiator when exposed to radiation generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

58. The laminated structure of Claim 56, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

59. The laminated structure of Claim 56, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

60. A method of laminating a structure, providing a structure comprising at least two layers, in which at least one layer is a cellulosic or polyolefin nonwoven web or film, with an adhesive composition between said layers, and irradiating the adhesive composition to cure the adhesive composition, wherein the adhesive composition comprises a photoreactor admixed with an unsaturated polymerizable material, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5.

61. The method of Claim 60, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species selected from the group consisting of a free radical, carbene, nitrene, anion, and cation.

62. The method of Claim 60, wherein the wavelength-specific sensitizer is selected from a group consisting of a moiety which is a phthalic acid derivative, and a moiety which is a phenyl-substituted aliphatic ketone derivative.

63. The adhesive of Claim 60, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

64. A polymer-coated fiber, produced by the process of: providing a fiber coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and irradiating the coating on the fiber with an amount of radiation sufficient to cure the composition.

65. The polymer-coated fiber of Claim 64, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

66. The polymer-coated fiber of Claim 64, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

67. The polymer-coated fiber of Claim 64, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

68. The polymer-coated fiber of Claim 64, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

69. The polymer coated fiber of Claim 64 wherein the photoreactor has a quantum yield greater than about 0.5.

70. A polymer-coated fiber, produced by the process of:
providing a fiber coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5; and

irradiating the coating on the fiber with an amount of radiation sufficient to cure the composition.

71. The polymer-coated fiber of Claim 70, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

72. The polymer-coated fiber of Claim 70, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

73. The polymer-coated fiber of Claim 70, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

74. A method of coating a fiber, comprising:
providing a fiber coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5; and

irradiating the coating on the fiber with an amount of radiation sufficient to cure the composition.

75. The method of Claim 74, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

76. The method of Claim 74, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

77. The method of Claim 74, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

78. A method of coating a fiber, comprising:
providing a fiber coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and
irradiating the coating on the fiber with an amount of radiation sufficient to cure the composition.

79. The method of Claim 78, wherein the unsaturated polymerizable material is an unsaturated oligomer/monomer mixture.

80. The method of Claim 78, wherein a spacer molecule is located between the wavelength-specific sensitizer and the reactive species-generating photoinitiator.

81. The method of Claim 78, wherein the reactive species-generating photoinitiator when irradiated generates a reactive species that is a free radical, carbene, nitrene, anion, or cation.

82. The method of Claim 78, wherein the wavelength-specific sensitizer is a phthalic acid derivative, or a phenyl-substituted aliphatic ketone derivative.

83. The method of Claim 78 wherein the photoreactor has a quantum yield greater than about 0.5.

84. A polymer-coated web, produced by the process of:
providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and
irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

85. The polymer coated web of Claim 84 wherein the photoreactor has a quantum yield greater than about 0.5.

86. A polymer-coated web, produced by the process of:
providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5; and
irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

87. A method of coating a web, comprising:

providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the wavelength-specific sensitizer has a molar extinction coefficient greater than about 5,000 liters per mole per cm at an absorption maximum; and irradiating the coating on the web with an amount of radiation sufficient to cure the composition.

88. The method of Claim 87 wherein the photoreactor has a quantum yield greater than about 0.5.

89. A method of coating a web, comprising:

providing a web coated with a composition comprising an admixture of unsaturated polymerizable material and a photoreactor, wherein the photoreactor comprises a wavelength-specific sensitizer covalently bonded to a reactive species-generating photoinitiator, and wherein the photoreactor has a quantum yield greater than about 0.5; and

irradiating the coating on the web with an amount of radiation sufficient to cure the composition.